



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|---|-----------|--|
| (51) International Patent Classification ⁵ : C08F 2/38, 4/52, 210/00 | A1 | (11) International Publication Number: WO 92/15619 (43) International Publication Date: 17 September 1992 (17.09.92) |
| (21) International Application Number: PCT/US92/01820 (22) International Filing Date: 3 March 1992 (03.03.92) (30) Priority data: 664,158 4 March 1991 (04.03.91) US Not furnished 21 February 1992 (21.02.92) US (71) Applicant: PHILLIPS PETROLEUM COMPANY [US/ US]; Bartlesville, OK 74004 (US). (72) Inventor: STRICKLEN, Phil, Marvin ; 1215 Hampden Road, Bartlesville, OK 74006 (US). (74) Agents: WEST, Paul, B. et al.; Ladas & Parry, 26 West 61 Street, New York, NY 10023 (US). | | (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> |
| (54) Title: PROCESS FOR PREPARING POLYOLEFINS HAVING A BIMODAL MOLECULAR WEIGHT DISTRIBUTION (57) Abstract <p>A two-step polymerization process for producing a polyolefin having a bimodal molecular weight distribution is provided. In step one, under polymerization conditions, at least two different alpha-olefins are contacted with a catalyst system which comprises an aluminosilicate and a metallocene, selected from the group consisting of mono, di, and tri-cyclopentadienyls and substituted cyclopentadienyls, of a metal selected from titanium, vanadium, chromium, zirconium, niobium, molybdenum, hafnium, tantalum, and tungsten, provided however if said metal is titanium then a metallocene of at least one other of said metals is present such that a first polymerization mixture is formed which comprises a low crystallinity, high molecular weight, copolymer, unreacted monomer, unreacted comonomer, and catalyst. This is followed by contacting, under polymerization conditions, hydrogen (and optionally additional alpha-olefin), with said first polymerization mixture which comprises copolymer, unreacted monomer, unreacted comonomer, and catalyst, such that a second polymerization mixture is formed which comprises a low crystallinity, high molecular weight copolymer, and a high crystallinity, low molecular weight homopolymer.</p> | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|----|--------------------------|----|--|----|--------------------------|
| AT | Austria | FI | Finland | ML | Mali |
| AU | Australia | FR | France | MN | Mongolia |
| BB | Barbados | GA | Gabon | MR | Mauritania |
| BE | Belgium | GB | United Kingdom | MW | Malawi |
| BF | Burkina Faso | GN | Guinea | NL | Netherlands |
| BG | Bulgaria | GR | Greece | NO | Norway |
| BJ | Benin | HU | Hungary | PL | Poland |
| BR | Brazil | IE | Ireland | RO | Romania |
| CA | Canada | IT | Italy | RU | Russian Federation |
| CF | Central African Republic | JP | Japan | SD | Sudan |
| CG | Congo | KP | Democratic People's Republic of Korea | SE | Sweden |
| CH | Switzerland | KR | Republic of Korea | SN | Senegal |
| CI | Côte d'Ivoire | LI | Liechtenstein | SU | Soviet Union |
| CM | Cameroon | LK | Sri Lanka | TD | Chad |
| CS | Czechoslovakia | LU | Luxembourg | TG | Togo |
| DE | Germany | MC | Monaco | US | United States of America |
| DK | Denmark | MG | Madagascar | | |
| ES | Spain | | | | |

- 1 -

PROCESS FOR PREPARING POLYOLEFINS HAVING A BIMODAL MOLECULAR WEIGHT DISTRIBUTION

This invention relates to a process for preparing polyolefins having a bimodal molecular weight distribution.

Polyolefins which have a bimodal molecular weight distribution have advantages over typical polyolefins which lack such bimodal molecular weight distributions. For example, while polyolefins can be made into articles by a number of various methods, polyolefins having a bimodal molecular weight distribution can be processed more easily. That is, they can be processed at a faster rate and with a lower energy requirement. Additionally, these polymers evidence a reduced melt flow perturbation and are thus preferred for such applications as high strength films. There are several known methods of producing polyolefins having a bimodal molecular weight distribution. However, each method has its own disadvantages. For example, polyolefins having a bimodal molecular weight distribution can be made by employing two distinct and separate catalysts in the same reactor. However, this process is subject to possible separation of the polyolefin mixture into nonhomogenous phases during storage and transfer of the polymer.

U.S. Patent 4,530,914 discloses a method of producing polyethylene having a broad molecular weight distribution or a multimodal molecular weight distribution. This polyethylene is obtained directly from a single polymerization process in the presence of a catalyst system comprising aluminoxane and two or more

- 2 -

metallocenes wherein each metallocene has a different propagation and termination rate. However, there are certain limitations to these types of methods for preparing bimodal molecular weight distribution polymers. For example, at certain ratios and in certain polymerization processes, even catalysts having aluminoxane and two different metallocenes can produce polyolefins which have a monomodal molecular weight distribution. Even under ideal conditions, if the bimodal molecular weight distribution of the polyolefin needs to be changed, a new catalyst needs to be made at different metallocene ratios.

One of the main applications of polyolefins is in the area of high strength films. It is highly desirable when making a polyolefin for high strength film applications that it be composed of two major components. The first component should be a high molecular weight component which has low crystallinity. The second component should be a low molecular weight component which has high crystallinity. The combination of these two components can produce a film with superior properties and thus would be both valuable scientifically and economically.

In accordance with the present invention, a two-step process for producing polyolefins having a bimodal molecular weight distribution is provided. In step one, at least two different alpha-olefins are contacted, under polymerization conditions, with a catalyst system comprising: at least one aluminoxane compound; and at least one metallocene compound, selected from the group consisting of mono, di, and tri-cyclopentadienyls and substituted cyclopentadienyls, or mixtures thereof, of a metal selected from the group consisting of titanium, vanadium, chromium, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, or mixtures thereof, provided that, at least one of the metallocene compounds utilized has the ability to form

- 3 -

essentially a homopolymer in the presence of hydrogen with said alpha-olefins and furthermore has the ability to form essentially a copolymer in the absence of hydrogen with said alpha-olefins; to form a first polymerization mixture. In step two, the first polymerization mixture is contacted, under polymerization conditions, with hydrogen to form a second polymerization mixture, from which a bimodal polyolefin can be recovered.

According to this invention, if said metal of the metallocene is titanium, then a metallocene of at least one other of said metals is present. The first polymerization mixture generally comprises a low crystallinity, high molecular weight, copolymer, unreacted monomer, unreacted comonomer, and catalyst. The first polymerization mixture is contacted, under polymerization conditions, with hydrogen (and optionally additional alpha-olefin) such that a second polymerization mixture is formed which generally comprises a low crystallinity, high molecular weight copolymer, and a high crystallinity, low molecular weight homopolymer.

DETAILED DESCRIPTION OF THE INVENTION

Catalyst System

Aluminoxanes are known in the art and are polymeric aluminum compounds which can be represented by the general formula $(R-Al-O)_n$ which is a cyclic compound and $R(R-Al-O)_nAlR_2$, which is a linear compound. In the general formula, R is a C_1-C_{10} , preferably a C_1-C_5 alkyl group such as methyl, ethyl, propyl, butyl, and pentyl, etc., most preferably, R is methyl, and n is preferably an integer of 1 to about 20.

It is known to prepare aluminoxanes by saturating an organic solvent with water which then reacts with the aluminum alkyl and forms aluminoxane. However, the water molecules in this process tend to cluster, which can over-hydrolyze the alkyl aluminum,

- 4 -

forming inactive Al_2O_3 thereby wasting reactants. A preferred method of adding water to hydrolyze the aluminum alkyl is to bubble an inert gas, such as nitrogen, saturated with water through a solution of the aluminum alkyl. The amount of water and the rate at which it is added can be controlled by the water temperature and the inert gas flow rate. The water is well dispersed thereby minimizing the formation of alumina (Al_2O_3). In this preferred process of making the catalyst there are fewer steps and no by-products produced that need to be removed before the aluminoxane can be used and furthermore the aluminum alkyl reactant is not wasted in the formation of alumina.

According to the invention, it is important that the metallocene have a different termination rate constant with respect to olefin polymerization in the presence of hydrogen. Such rate constants can be determined by one of ordinary skill in the art. It is essential in this invention, that the metallocene chosen, when in the presence of hydrogen, makes essentially homopolymer whereas in the absence of hydrogen, this same metallocene essentially makes a copolymer. In general, the metallocenes employed in accordance with this invention are represented by the general formula $(\text{C}_5\text{R}'_m)_p \text{R}''_s (\text{C}_5\text{R}'_m)_p \text{MeQ}_3$ and $\text{R}''_s (\text{C}_5\text{R}'_m)_2 \text{MeQ}'$ wherein: each $(\text{C}_5\text{R}'_m)$ is a cyclopentadienyl or a substituted cyclopentadienyl group; each R' can be independently selected from the group consisting of hydrogen and hydrocarbyl radicals wherein the hydrocarbyl radicals are selected from the group consisting of alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radicals which have from about 1 to about 20 carbon atoms per radical, additionally, the R' can be independently selected from adjacent carbon atoms which are joined together to form a C_4 - C_6 ring; each R'' is selected from the group consisting of C_1 - C_4 alkylene

- 5 -

radical, dialkyl germanium, dialkyl silicone, alkyl phosphine, or amine radical which bridges two $(C_5R'_m)$ rings; each Q is independently selected from the group consisting of halogens, or hydrocarbon radicals selected from the group consisting of aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radicals each having from about 1 to 20 carbon atoms; each Q' is an alkylidene radical having from 1 to about 20 carbon atoms; Me is a transition metal selected from the group consisting of titanium, vanadium, chromium, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten; s is 0 or 1; p is 0, 1 or 2; when p is 0, s is 0; m is 4 when s is 1 and m is 5 when s is 0.

It is preferred that the metallocene be a cyclopentadienyl of zirconium. Cyclopentadienyl complexes of zirconium form very effective and active catalysts with aluminoxanes. The dimethyldicyclopentadienyl complexes of zirconium are more preferred due to their ease of preparation and the fact that they are free from chlorides, making the catalyst system totally halogen free. Furthermore, the zirconium catalyst is more susceptible to the presence of hydrogen than other similar metallocenes. Specifically, the zirconium catalyst in the presence of hydrogen and two different monomers will tend to make a homopolymer of one of the monomers, whereas the same catalyst in the absence of hydrogen and in the presence of the same two monomers will tend to make a copolymer of these two monomers. In contrast, titanium is unaffected by the presence or absence of hydrogen in this polymerization process. Thus, if a titanium metallocene is used it must be used in combination with a metallocene of one of the other metals, preferably zirconium.

It is preferred that the metallocene is contacted with a soluble aluminoxane to form a catalyst. It is also possible, and even more preferred, to react a

- 6 -

reactant mixture of the metallocene with the aluminum alkyl in a hydrocarbon solvent followed by bubbling a wet inert gas through the mixture to hydrolyze the aluminum alkyl thereby producing a polymerization catalyst.

If the hydrocarbon is an aliphatic hydrocarbon, the aluminoxane as it is formed will precipitate. It is preferred that if the aluminoxane is prepared prior to the addition of the metallocene that the hydrocarbon solvent be aromatic so that the aluminoxane will remain in solution until after reacting with the metallocene. If, however, the metallocene is present with the aluminum alkyl prior to the formation of aluminoxane it is preferred that the hydrocarbon solvent be an aliphatic hydrocarbon so that upon formation of the aluminoxane, the catalyst precipitates.

The most preferred process of preparing the catalyst essentially comprises: bubbling a wet inert gas through a mixture of (a) an aliphatic hydrocarbon solvent; (b) an amount of an aluminum compound of the formula AlR_3 wherein each R can be the same or different and is selected from alkyl groups having from 1 to 10 carbon atoms; and (c) cyclopentadienyls and substituted cyclopentadienyls of a transition metal which is sensitive to the presence of hydrogen in this polymerization process; thereby producing a solid melt on aluminoxane polymerization catalyst wherein the temperature and pressure of said mixture is sufficient to maintain said hydrocarbon solvent in liquid phase and produce said catalyst.

In the process of preparing the catalyst it is preferred, but not required, that the inert gas be saturated with water. When the particular inert gas is saturated with water it is easier to calculate how much water has reacted with the aluminum alkyl. It is important to know how much water has reacted so that the aluminum alkyl is not converted to alumina by having too

- 7 -

much water present.

It is preferred that the inert gas be bubbled through the water at a temperature, pressure, and rate to essentially saturate the inert gas with water which is followed by bubbling this wet inert gas through the hydrocarbon solvent, containing the reactants, at a temperature, pressure, and rate sufficient to react the water in the inert gas with the aluminum alkyl compound. It is preferred that the molar ratio of water to aluminum alkyl, that is bubbled through the hydrocarbon solvent in the inert gas, be within the range of about 0.01:1 to 1.4:1, more preferably within the range of about 0.5:1 to 1:1. Furthermore, the inert gas can be any non-reactive gas, such as nitrogen or the noble gases in group VIII of the Periodic Table of the elements. Nitrogen is most preferred due to its availability. Additionally, it is preferred that the weight ratio of aluminum alkyl to hydrocarbon be within the range of about 1:1 to 1:100, preferably about 1:2 to 1:50, and most preferably about 1:4 to 1:10. Lastly, it is preferred that the hydrocarbon be selected from normal and cyclo alkanes having from 5 to 10 carbon atoms, n-hexane being preferred.

In this invention, it is preferred that the aluminum alkyl (AlR_3) be an aluminum alkyl wherein each R is selected from alkyl groups having 1 to 5 carbon atoms. The most preferred aluminum alkyl being trimethyl aluminum. Furthermore, it is preferred that the aluminoxane support/cocatalyst make up the majority of the catalyst. Preferably the weight ratio of total metallocenes to aluminoxane is within the range of about 1:5 to about $1:10^8$, preferably about 1:10 to $1:10^5$, and more preferably 1:20 to $1:10^3$.

Reaction Conditions

According to the invention it is preferred that the polymerization process be conducted under slurry phase polymerization conditions. It is preferred

- 8 -

that the slurry phase polymerization conditions, in both polymerization steps, comprise: a polymerization temperature from about 80°C. to about 110°C.; a polymerization pressure from about 250 psia to about 700 psia, preferably it is from about 400 psia to about 600 psia, and most preferably it is from 500 to 565 psia; a polymerization time from about 1 minute to about six hours; preferably from about 10 minutes to about two hours, and most preferably from 20 minutes to 1 hour.

10 In the process of the present invention it is preferred that the weight ratio of diluent to catalyst be within the range of about 500:1 to 1,000,000:1, preferably about 1,000:1 to 100,000:1, and more preferably 2,000:1 to 10,000:1. It is preferred that
15 the polymerization reaction be run in a diluent at a temperature at which the polymer remains a solid in the diluent. Diluents include, for example, isobutane, n-hexane, n-heptane, and methylcyclohexane, etc. The preferred diluent is isobutane. These conditions also
20 apply to both steps.

The monomers that are used in the process of the present invention are preferably selected from alpha olefins, preferably alpha-olefins having from 2 to 10 carbon atoms. More preferably, these alpha-olefins are
25 selected from the group consisting of ethylene, propylene, 1-hexene, and mixtures thereof, ethylene being the most preferred. It is preferred that the comonomer for the production of the copolymer be a alpha-olefin which has from about 3 to about 10 carbon
30 atoms. More preferably, the comonomer is selected from the group of 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, or mixtures thereof. Most preferably the comonomer is 1-hexene. The weight ratio of monomer to comonomer, in the first step, should be in the range of
35 about 95 to 5, for example, when producing a ethylene-1-hexene copolymer the ratio of ethylene to 1-hexene should be 95 parts by weight ethylene to 5 parts by

- 9 -

weight 1-hexene based on 100 total parts of monomer and comonomer. More preferably, the ratio is 99 parts by weight monomer to 1 part by weight comonomer and most preferably it is 99.4 parts by weight monomer to .6 parts by weight comonomer. These ratios tend to give the optimum productivity for producing copolymers. Generally, the entire amount of comonomer is added during the first polymerization, but in any event the above ratio represent the total amount.

The monomers used in this invention include, but are not limited to, ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene, 1-heptene, 1-octene, 1-decene, and mixtures thereof. The comonomers used in this invention include, but are not limited to, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene, 1-heptene, 1-octene, 1-decene, and mixtures thereof.

According to the invention it is preferred that the relative amounts of hydrogen introduced in the second polymerization step be within the range of about 0.001 to 15 mole percent hydrogen and 99.999 to 85 mole percent olefin based on total hydrogen and monomer present, preferably 1 to 10 mole percent hydrogen and 99 to 90 mole percent monomer. The amounts of about 4 mole percent hydrogen and 96 mole percent monomer. The amounts of about 4 mole percent hydrogen and 96 mole percent monomer being most preferred because the polymer produced by this mixture is of the appropriate molecular weight to give the most desired polymer properties.

Process of the Invention

The catalyst system and two different monomers are placed in a polymerization zone under polymerization conditions. It is important that there be essentially no hydrogen present during the first polymerization step. This is to enhance the polymerization of a low

- 10 -

crystallinity, high molecular weight, copolymer. The resulting polymerized mixture comprising copolymer, unreacted monomer, unreacted comonomer, catalyst and diluent is then contacted with hydrogen in the second polymerization step and allowed to polymerize further. This facilitates the production of a high crystallinity, low molecular weight, homopolymer. This provides an essentially homogeneous product which has superior properties for such applications as film. The second polymerization step can be completed in the same zone by adding hydrogen in a batch type operation, or the polymerization mixture resulting from the first polymerization step can be introduced into a second polymerization zone under either batch or continuous conditions.

Reference to first and second polymerization steps does not exclude the possibility of three or more polymerization steps.

For the purposes of this application, the term "low crystallinity" means that the amount of crystallinity, as derived from density data collected in accordance with ASTM-D-1505, is less than or equal to 60%. The term "high crystallinity", for the purposes of this application, means that the amount of crystallinity, as derived from density data collected in accordance with ASTM-D-1505, is greater than 60%. Also for the purposes of this application, the term "high density", in relation to polyethylene, means a density greater than or equal to 0.94 grams per cubic centimeter. Additionally, the term "low density", in relation to polyethylene, means a density less than 0.94 grams per cubic centimeter. The term "high molecular weight", for the purposes of this application means a weight average molecular weight equal to or greater than 100,000, as determined from size exclusion chromatography. The term "low molecular weight", for the purposes of this application means a weight average

- 11 -

molecular weight less than 100,000, as determined from size exclusion chromatography.

EXAMPLES

These examples are provided to further assist a person skilled in the art with understanding this invention. The particular reactants, conditions, and the like, are intended to be merely illustrative of this invention and are not meant to be construed as unduly limiting the reasonable scope of this invention.

The catalyst was prepared in the following manner. To a 250 ml crown capped bottle the following were added, 0.198 grams of $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ (bis(cyclopentadienyl) dimethyl zirconium), and 0.84 grams of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ (bis(cyclopentadienyl) dimethyl titanium), dissolved in 12 mls of toluene. The solution was diluted to 100 mls with n-hexane and 1.69 g trimethyl aluminum was added as a 25 weight percent solution in n-hexane. Nitrogen was slowly bubbled through the solution with vigorous stirring. A precipitate gradually formed as the color changed from yellow green to a brick red. The solid was filtered in a dry box and washed with n-hexane.

Run 1

To a 2-liter autoclave reactor the following was charged: 1) the catalyst made above; 2) 1-liter of isobutane; 3) 18 grams of 1-hexene. The reactor was then pressurized to 350 psia with ethylene. The temperature was raised to 90°C. and the reaction was allowed to continue for 100 minutes. During the polymerization an additional 4.33 grams of 1-hexene was added. The isobutene was flashed at the end of the production run and the polymer was recovered as a free flowing powder. The physical properties of the polymer are recorded in Table I.

Run 2

Run 2 was conducted in the same manner as Run 1 except that 40 grams of 1-hexene was added at the

- 12 -

beginning of the trial and 7.86 grams of 1-hexene was added during the run. However, in contrast to Run 1 this reaction was allowed to proceed for 120 minutes. The physical properties of this polymer are also recorded in Table I.

Run 3

This polymerization was conducted in the same manner as Example I except 4.17 grams of hexene was added during the run and 20 psia of hydrogen was added at the beginning of the run. The run was allowed to proceed for 50 minutes before procedures for recovering the polymer were implemented. The physical properties of the polymer are recorded in Table I.

Run 4

This polymerization was conducted as in Run 2 except that 20 psia of hydrogen was added at the beginning of the run. Additionally, the run time was only 70 minutes. The physical properties of this polymer are recorded in Table I also.

TABLE I¹

| Run Number | Density | Melt Index | High Load Melt Index | M _n | M _w | HI |
|------------|---------|------------|----------------------|----------------|----------------|------|
| 1 | 0.9296 | 0.053 | 1.1 | 24,800 | 196,000 | 7.9 |
| 2 | 0.9259 | 0.12 | 2.7 | 29,720 | 172,910 | 5.8 |
| 3 | 0.9526 | 5.4 | 224 | 5,440 | 67,350 | 12.9 |
| 4 | 0.9519 | 3.5 | 211 | 5,140 | 70,980 | 13.8 |

¹The density was determined in accordance with ASTM D1505. The melt index values were determined by ASTM Standard D1238 Condition D. The high load melt index values were determined by ASTM Standard D1238 Condition F. The number average molecular weight (M_n), the weight average molecular weight (M_w), and the heterogeneity index (HI) were all determined by size exclusion chromatography (SEC).

In Runs 1 and 2, no hydrogen was added to the reactor and a low crystallinity, high molecular weight, copolymer was produced. The low crystallinity in Runs 1

- 13 -

and 2 is evidenced by the low density of the polymer. In Runs 3 and 4, hydrogen was added to the reactor thus producing a high crystallinity, low molecular weight, polymer. The high crystallinity in Runs 3 and 4 is
5 evidenced by the high density of the polymer. The high densities were achieved even though the same amount of comonomer was present in these runs as was present in runs 1 and 2 which produced low density polymer. Consequently, if these runs were performed sequentially,
10 that is, the procedure in Run 1 was accomplished followed by the procedure in Run 3, a bimodal molecular weight distribution product having a high molecular weight, low crystallinity, copolymer and a low molecular weight, high crystallinity, homopolymer, would be
15 produced and would provide a homogeneous blend of the two polymers.

- 14 -

C L A I M S

1. A process for producing polyolefins having a bimodal molecular weight distribution which comprises:
 - (A) contacting under polymerization conditions
 - (1) at least two different alpha-olefins;
with
 - (2) a catalyst system comprising
 - (a) at least one aluminoxane compound,
and
 - (b) at least one metallocene compound
which is a mono, di, or tri-
cyclopentadienyl, a substituted
cyclopentadienyl, or a mixture
thereof, of a metal which is
titanium, vanadium, chromium,
zirconium, niobium, molybdenum,
hafnium, tantalum, tungsten, or a
mixture thereof, provided that, at
least one of the metallocene
compounds utilized has the ability
to form essentially a homopolymer
in the presence of hydrogen with
said alpha-olefins and furthermore
has the ability to form essentially
a copolymer in the absence of
hydrogen with said alpha-olefins;
to form a first polymerization mixture; followed by
 - (B) contacting under polymerization conditions
 - (1) said first polymerization mixture;
with
 - (2) hydrogen;
to form a second polymerization mixture.
 2. A process according to claim 1, wherein said metallocene is of titanium and a metallocene of at least one other of said metals is present.
 3. A process according to claim 1 or 2, wherein said first polymerization mixture comprises a low crystallinity,

- 15 -

high molecular weight, copolymer and said second polymerization mixture comprises said low crystallinity, high molecular weight copolymer, and a high crystallinity, low molecular weight homopolymer.

4. A process according to any one of claims 1-3, wherein said polymerization conditions comprise slurry phase polymerization conditions.

5. A process according to claim 4, wherein said slurry phase polymerization conditions comprise a temperature of about 80°C. to about 110°C.

6. A process according to claim 4 or 5, wherein said slurry phase polymerization conditions comprise a pressure of about 250 psia to about 700 psia.

7. A process according to any one of claims 4-6, wherein said slurry phase polymerization conditions comprise a polymerization time of about 1 minute to about 6 hours.

8. A process according to any one of the preceding claims, wherein said at least two different alpha-olefins comprise at least two of ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene, 1-heptene, 1-octene, and 1-decene.

9. A process according to claim 8, wherein said at least two different alpha-olefins are ethylene and 1-hexene.

10. A process according to claim 9, wherein the first polymerization mixture and the hydrogen are further contacted with additional ethylene.

11. A process according to any one of the preceding claims, wherein the aluminoxane compound is methyl aluminoxane.

12. A process according to any one of the preceding claims, wherein the metallocene compound comprises bis(cyclopentadienyl) dimethyl zirconium.

13. A process according to claim 12, wherein the metallocene compound further comprises bis(cyclopentadienyl) dimethyl titanium.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/01820

| | | |
|--|---|---|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ | | |
| According to International Patent Classification (IPC) or to both National Classification and IPC | | |
| IPC (5): C08F 2/38, 4/52, 210/00 | | |
| U.S. CL: 525/247, 268, 319; 526/82, 114, 116, 119, 160 | | |
| II. FIELDS SEARCHED | | |
| Minimum Documentation Searched ⁷ | | |
| Classification System | Classification Symbols | |
| U.S. | 525/247, 268, 319; 526/82, 114, 116, 119, 160 | |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸ | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ | | |
| Category ¹⁰ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
| Y | US, A, 4,530,914 (EWEN ET AL) 23 JULY 1985 See column 2, lines 5-45 and column 3, lines 3-9. | 1-3 |
| <u>X</u> Y | US, A, 4,701,432 (WELBORN, JR.) 20 OCTOBER 1987; See column 2, line 65 to column 3, line 9, column 3, lines 31-38, column 9, lines 31-68 and Examples 1-5. | <u>1-3</u> 1-3 |
| Y | US, A, 4,937,299 (EWEN ET AL) 26 JUNE 1990 See column 2, lines 3-19 and column 2, line 28 to column 3, line 15. | 1-3 |
| X | US, A, 4,939,217 (STRICKLEN) 03 JULY 1990 See column 2, lines 27-51 and column 9, line 24 to column 11, line 63. | 1-3 |
| X,P | US, A, 5,032,562 (LO ET AL) 16 JULY 1991 See column 1, lines 23-49, column 2, lines 3-59 and column 9, lines 1-37. | 1-3 |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div> | | |
| IV. CERTIFICATION | | |
| Date of the Actual Completion of the International Search | | Date of Mailing of this International Search Report |
| 27 APRIL 1992 | | 27 MAY 1992 |
| International Searching Authority | | Signature of Authorized Officer |
| ISA/US | | Romulo Delmendo |

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ^{1,2} not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ^{1,3}, specifically:

3. ☒ Claim numbers 4-13, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.